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CLOSED CHAMBER BURNING CHARACTERISTICS OF NEW VHBR FORMULATIONS

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October 1985



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Combustion studies were carried out on VHBR propellants in order to determine formulation and fabrication parameters that control the burning characteristics of these compounds. Formulation parameters such as type of fuel, oxidizer, type and percent of binder, oxidizer/binder ratio and percent of theoretical maximum density were varied and the effects on combustion were studied using both a closed chamber and an optically transparent bomb.

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20. ABSTRACT (Con't)

Although numerous facets of the combustion mechanisms remain unclear, the following picture has emerged for the specific formulations studied. The first phase of combustion is a relatively slow porous burning that proceeds down throughout the sample. The original form of the sample remains, although the residue is porous and is filled with hot combustion products. Depending on the composition, percent theoretical density and sample confinement, a transition to a very rapid combustion takes place throughout the entire sample, accompanied by some deconsolidation. For some conditions (composition or confinement) this second phase does not occur. The transition pressure to and the velocity of the second phase varies with the formulation parameters. The details of these results are discussed in the remainder of the paper.

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I. INTRODUCTION

Successful performance of a traveling charge gun requires propellants with very high burning rate characteristics, much greater than conventional propellants. A new class of very high burning rate (VHBR) propellants are now under development. The purpose of this work is to estimate the suitability of new boron-hydride formulations for this purpose and to understand the mechanisms that control the burn rates of these materials.

This report describes closed chamber studies of the combustion characteristics of several VHBR formulations. Additionally, tests were carried out in an optically transparent chamber using high speed cinematography and time correlated pressure measurements. These techniques help characterize the burning characteristics of VHBR compounds.

II. CLOSED CHAMBER STUDIES

A. Experimental

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Closed chamber combustion studies were carried out on numerous new formulations at loading densities of approximately 0.08 g/cm³. Samples, as received, were in the form of cylinders or slabs. For all tests, samples were end ignited with an Atlas, M100 electric match and 1 g of class 6 black powder (FFFG). Samples, at first, were inhibited on the sides with asphaltum. As in previous studies² it was found that circumferential confinement of the sample was very important in obtaining rapid burning rates. Consequently most of the tests were conducted with 12.5-mm diameter, 25.4-mm long samples mounted in steel sleeves, with a wall thickness of either 1.2 mm, or 3.2 mm, in a closed chamber of volume 54.5 cm³. The samples were held in place using a liberal application of slow-curing epoxy. The samples which were in the form of slabs were trimmed, coated with epoxy and fitted into the standard sleeves. The experimental set-up is shown in Figure 1.

Pressure measurements were made using Kistler 607C3 and 607C4 transducers along with Kistler 504E charge amplifiers. Data were acquired using dual Nicolet Explorer III digital oscilloscopes. Data were then transferred to a PDP 11/34 minicomputer. Propellant burn rates were calculated using the CBRED 2^2 program, assuming end burning of the samples.

The samples used in this study are identified in Table 1, which lists the details of the composition and their density as a percent of theoretical maximum density (TMD). The reasoning governing the choice of composition and

²A.A. Juhasz, I.W. May, W.P Aungst and F.R. Lynn, "Combustion Studies of Very High Burning Rate (VHBR) Propellants," Ballistic Research Laboratory Memorandum Report, ARBRL-MR-03152, February 1982.



A.A. Juhasz, S.T. Peters, R.E. Hanson and L.K. Asaoka, "Development of VHBR Propellant Formulations with Improved Safety Characteristics," 21st JANNAF Combustion Meeting, Johns Hopkins University/ Applied Physics Laboratory, Laurel MD, 1-5 October 1984.

B. Results

Table 2 gives the results of closed chamber firings for a large number of compounds defined in Table 1. This table contains the sample ID, loading density, measured maximum pressure (Pmax), the percent of the calculated Pmax, rise time from 16-90% of Pmax, and the transition pressure which will be discussed later. No calculations for Column 4 were carried out for samples TC-003-011. Rise time was chosen as the measurement to compare compositions. Nominal average burn velocities can be estimated using these rise times and sample dimensions. Also, burn rates can be determined by standard closed chamber reduction techniques. However, both of these calculations assume a laminar cigarette-type burning of the compound. A later section will show that this is probably not the case. Furthermore, it has been observed both in this study and previous ones that the pressure measured in the chamber by the gauge is not the same as the pressure at the burning surface. This is shown by the fact that the steel sleeves surrounding the samples are badly distorted during the burning of the fast samples. Thus, the pressure internal to the sleeve is not the same as measured by the gauge at the chamber wall. Nevertheless, it is instructive to calculate apparent burn rates as a function of chamber pressure for comparison of formulations and evaluating reproducibility.

An example of a pressure-time history is shown in Figure 2. A very sharp discontinuity is observed at approximately 130 ms. This is defined as a transition pressure, and is listed in Table 2. The rise time is measured beyond this transition. This abrupt change was not always observed, especially for the slower burning compounds. Burn rates were calculated using data that were beyond this transition point.

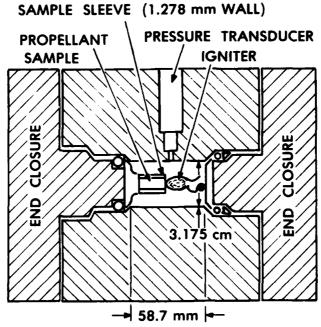


Figure 1. Closed Chamber Configuration for VHBR Studies

TABLE 1. VHBR PROPELLANT FORMULATIONS

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	Sample ID	Fuel-	(x)	Oxidizer-	LLANT FORM (Z)	VHBR PROPELLANT FORMULATIONS Oxidizer- (2) Binder -	8	THD (Z)
	1086-78	997Н	10.5	TAGN	84.5	C4000	2.0	98.0.88.0
	TC-014 TC-015 TC-016	H466 H466 H466	12.0 12.0 12.0	RDX RDX RDX	73.0 78.0 83.0	KRATON KRATON KRATON	15.0 10.0 5.0	99.4,96.0,91.2 98.3,95.0,89.3 98.0,93.5,89.0
	TC-007 TC-008 TC-003	H466 H466 H466	12.3 12.0 12.0	TAGN RDX RDX	59.4 60.0 74.0	HTPB HTPB KRATON	28.3 28.0 14.0	98.2
	TC-010 TC-004	H498 H498	10.9 15.0	RDX RDX	63.8	HTPB KRATON	25.3 15.0	100.0**
9	TC-011 TC-009	H498 H466	13.2	TAGN	55.0 51.4	HTPB HTPB	31.8 33.0*	
	TC-020	H498	15.0	TAGN	30.0 50.0	GAP NC BDNPA/F IPDI	1.7 0.2 2.3 0.8	**06

* Contained 4.4% phenolic microballons
** Nominal value

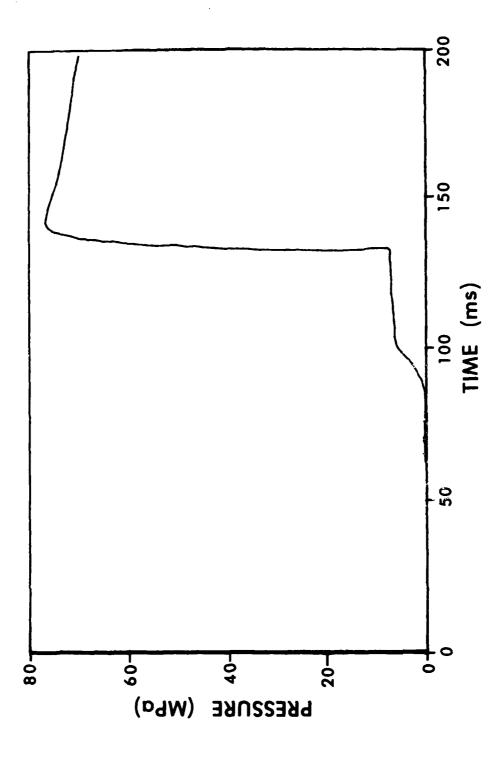


Figure 2. Pressure vs Time for Formulation TC-015 (95% TMD)

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TABLE 2. RESULTS OF CLOSED CHAMBER FIRINGS

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Transition Pressure(MPa)	N/A Unknown Unknown 10.3	none 5.40 5.80 6.20	6.40 6.10 5.60 4.70	6.80	none none none none none
Rise Time 16-90%Pmax (ms)	6000.0 35.0 20.0 18.0 0.7	175.0 33.0 12.0 133.0	44.0	21.0 (Thick Sleeve) <0.5 (Thick Sleeve)	1115.0 632.0 1145.0 2980.0 261.0 215.0 320.0
(%)Cal. Pmax	76 67 70 65	60 77 88 62	80 80 90	90 95 95	
Pmax (MPa)	N/A 72.65 63.63 76.96 66.21	56.42 77.30 79.02 67.07	82.82 84.02 100.77 103.24	115.44	28.94 40.37 33.42 40.72 55.95 65.24 40.58
(g/cc)	~ 0 0.079 0.079 0.080 0.081	0.083 0.082 0.077 0.085	0.084 0.083 0.091 0.087	0.095	0.072 0.086 0.079 0.087 0.083 0.096 0.069
Sample ID and nominal % TMD	78/88%TMD* 78/100%TMD** 78/88%TMD** 78/100%TMD	TC-014/100% TMD TC-014/95% TMD TC-014/90% TMD TC-015/100% TMD	TC-015/95%TMD TC-015/90%TMD TC-016/100%TMD TC-016/95%TMD	TC-016/100%TMD TC-016/90%TMD	TC-009 TC-010 TC-007 TC-008 TC-003/100%TMD TC-004/100%TMD TC-011

* Burned at ambient pressure ** Burned unconfined in the closed chamber

Several observations can be made from these data obtained from the standard CBRED 2 closed chamber burning rate reductions of the pressure time data. Reproducibility from run-to-run was at best, fair. This is influstrated in Figure 3, sample TC-016 (100% TMD). For conventional slow properties, reproducibility is on the order of 1 to 2%. In this case the scatter was from 10 to 15%. For the lower density, faster burning samples the scatter was larger.

Additionally, it was observed that the low density 1086-7B burned much slower (6 seconds) under ambient conditions, even when the side walls were confined. Consequently, for these compounds, pressure is required for rapid burning. Under closed chamber conditions with self-pressurization, confinement of the sides of the compound is also required for rapid burning. This is seen in Table II for formulation 1086-7B. Samples burned in the chamber without confinement burned substantially slower. As a consequence of these tests, all subsequent compounds were burned in a confined configuration.

The compounds identified as TC-014,015 and 016 form a family wherein the difference between them is in the percent binder. Table 1 shows that TC-014 contains 15% Kraton binder whereas TC-015 has 10% and TC-016 5% binder. There is a corresponding increase in the amount of RDX. All of these compounds were also pressed to 100%, 95% and 90% of the TMD. It is clearly shown that the burning velocity increases as both the %TMD and binder content decrease. An increase is also observed in the apparent burning rates and is shown in Figures 4 and 5.

Figure 4 illustrates an abnormal behavior for the burn rate which has also been observed in previous studies. The rate decreases as pressure increases. This is seen primarily for the fast burning compositions. The assumption in these calculations is that the propellant burns cigarette—fashion and that the surface area remains constant during the combustion process. In fact, if the sample were burning porously with subsequent deconsolidation, the surface area would start to decrease leading to an apparent decrease in calculated burning rate. This phenomena, due to form function mismatch, is sometimes observed in conventional multi-perf propellants when slivering occurs, i.e. when the perforations burn through. The surface area of the slivers decreases as they burn leading to an apparent computed decrease in burning rate. More discussion on porous burning will be given in the section entitled Optically Transparent Chamber.

As shown in Table 2, the effect of density is also observed with sample 1086-7B which was pressed at both 100% and 88% TMD. The latter burns in a much shorter time.

The degree of confinement also has an effect on the burn time and this is illustrated in Figure 6. In these runs, one sleeve had a wall thickness of 1.6 mm and the other 3.2 mm. The stronger confinement induces a faster burn possibly due to higher internal pressures permitted by the stronger sleeves.

Evidence of overpressure within the confining steel sleeves is shown in Figure 7. Generally, the degree of deformation of the sleeves increased with decreasing % TMD for a given composition. However, in one case (TC-016/95% TMD) the sample produced complete fracturing.

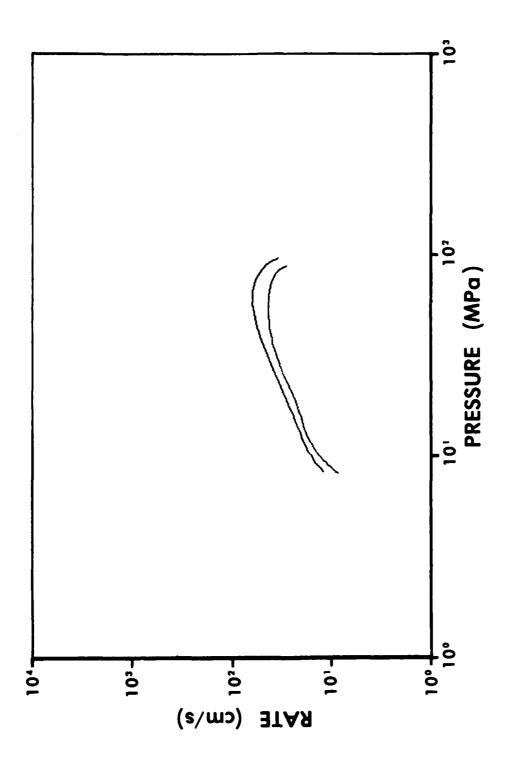


Figure 3. Apparent Burn Rate vs Pressure: Formulation TC-016 (100% TMD), Reproducibility Study

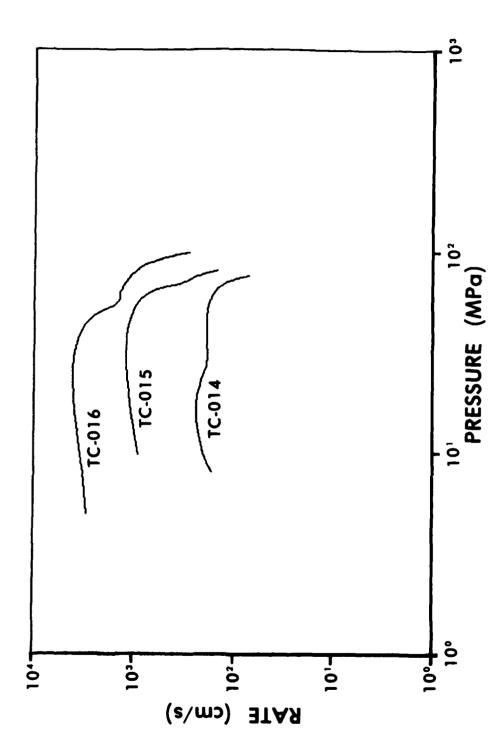


Figure 4. Comparison of Apparent Burning Rates for Formulations TC-014, 015 and 016 at 90% TMD

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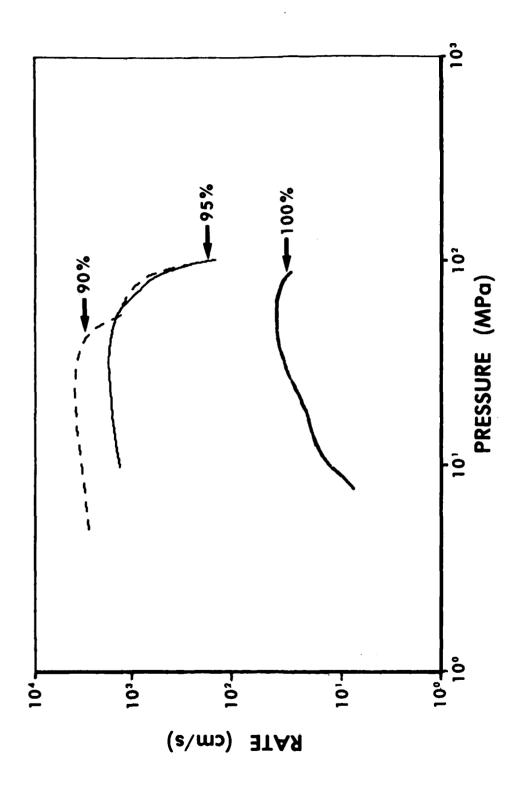


Figure 5. Comparison of Apparent Burning Rates for Formulation TC-016, 90%, 95% and 100% TMD

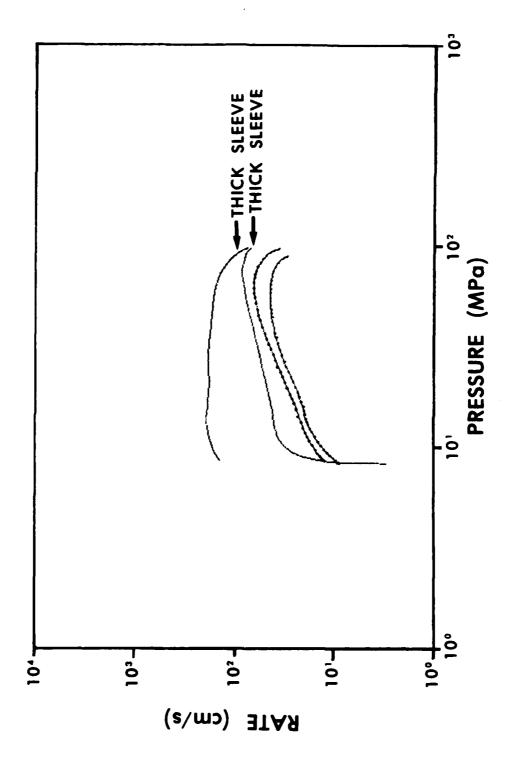


Figure 6. Effect of Confinement on Apparent Burning Rate;
Formulation TC-016 (100% IMD)
---- Thick Sleeve, 3.2 mm, ---- Thin Sleeve, 1.6 mm.



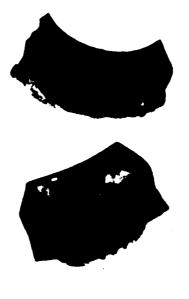
TC-015/95%TMD



TC-015/90%TMD



TC-016/90%TMD



TC-016/95%TMD

Figure 7. Post-firing Photographs of Confining Steel Sleeves

The last entry in Table 2 demonstrates the importance of composition. TC-014, 015 and 016 differ only in the binder content. Composition TC-020 contains an energetic binder. Formulations TC-014 thru 016 had an inerc binder, Kraton. Further the oxidizer in these formulations was RDX. For contrast, composition TC-020 had an active (energetic functionality) binder as well as an oxidizer composed of TAGN/HMX. Both the energetic binder and TAGN were used to increase in their burn rates. The burn time for this formulation was by far, the shortest measured for any of the formulations in this series. It should also be noted, that the transition pressure for this formulation was approximately 1/2 that of the other compounds. The speed of burning appears to correlate roughly with the transition pressure, i. e. the faster formulations have a lower transition pressure.

Formulations designated TC-007 through TC-011 gave very long rise times, from 300 ms to 3 seconds. These long times correlate with the high binder (and lower oxidizer) content which varied from 25 to 33 %.

Column 4 in Table 2 gives the percent of the calculated maximum pressure reached by the experimentally measured maximum pressure. A relatively low value is found for the slower burning formulations which may be attributed to a large heat loss. Nevertheless, even fast burning formulations such as 1086-78 (88% TMD) and TC-015 (90% TMD) substantially deviate from calculated values.

C. Conclusions

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The burn times of these samples under closed chamber conditions were found to depend on a number of factors:

Composition - burn times varied by several orders of magnitude depending on the composition. Increased solids loading, the use of Hivelite 498 (as opposed to Hivelite 466) and the use of an active binder, GAP (in place of Kraton, CTPE and HTPB) all aided in obtaining faster burning rates. The reasoning behind the choice of composition will be discussed in another paper. I

Density - densities were varied from 88% to 100% of the theoretical maximum density. Over this range of densities the burn times changed by more than a factor of 20.

Confinement - side confinement was found to be essential for rapid combustion. The degree of confinement was also found to be important as lightly confined samples burned slower than those confined in heavy-walled tubes.

Pressure - samples confined only on the sides and burned at ambient pressure yielded very low burn rates demonstrating the need for pressurization before rapid combustion can take place.

Transition pressure - for many samples, there appears to be a transition pressure where slow combustion changes to a more rapid combustion. This is generally no greater than 7 MPa. At this point one can only speculate on the nature of the chemical and physical causes for this observation.

III. OPTICALLY TRANSPARENT CHAMBER STUDIES

A. Experimental

To complement the closed chamber and x-ray transparent studies on these compounds, experiments were conducted employing a horizontally mounted, optically transparent chamber shown in Figure 8. The inside diameter of the plastic chamber was 12.5 mm, just large enough to accommodate the samples. The outside diameter was 50.8 mm. The chamber length was 130 mm giving a nominal loading density of approximately 0.25 g/cm³. The forward end of the chamber was fitted with a blow-out rupture disc consisting of two thicknesses of 0.48-mm aluminum. The blow-out pressure was calculated to be 21 MPa. The rupture pressure of the plastic chamber was calculated to be about the same, 21 MPa. The samples were ignited with an electric match, and 0.2 grams of Class 6 black powder.

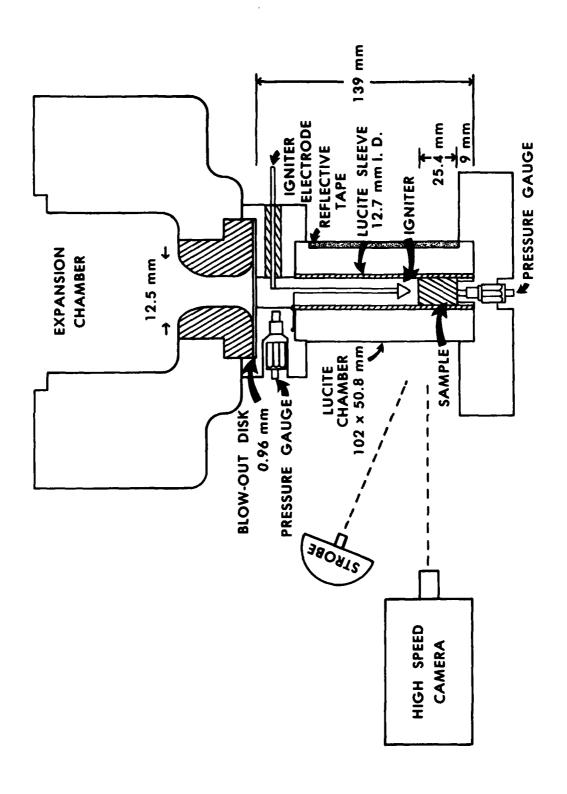
A pressure gauge was mounted in the forward section of the chamber, just before the rupture disc, 11.3 cm from the front surface of the sample. A second gauge was mounted at the rear of the chamber, beneath the end of the sample. Both gauges were recessed so as not to be impinged upon by solid particle combustion products. The sample was epoxied to the sides of the transparent plastic chamber, and to the bottom of the end wall containing the second gauge. On some tests the epoxy covered the end wall gauge hole, resulting in either a zero pressure reading, or a sudden jump in pressure when the apoxy film was ruptured by the rising pressure. Consequently, the first gauge was used as the primary data source. Time zero is defined as the time of application of the voltage to the electric match. For some measurements time zero is arbitrary, due to the triggering mode of the data acquisition system.

A high speed cinematography system was used to record photographic events at 5000 pictures per second. Thus the time between frames was 200 microseconds, and the exposure time for an individual frame was 80 microseconds. A strobe light source was used to provide external lighting to the chamber. This source had a pulse width of approximately 1.5 microseconds and was triggered by the camera to give lighting to every other frame. Thus, the resulting pictures consisted of alternate frames of self-illumination and external illumination. To increase contrast and visibility of the event, a reflecting tape was mounted on the plastic chamber wall, opposite to the camera.

B. Results

Numerous tests in the optically transparent chamber were carried out on the TC-014, 015 and 016 family of formulations. As seen from Table 1, they represent a systematic approach to studying the effects of formulation and density variation. Additionally, as seen in Table 2, the results from the closed chamber tests showed a systematic sequence of burn characteristics.

J. Trimble, R. Frey, K. White and A. Bines, "X-Ray Studies of the Combustion of Some VHBR Propellants," 21st JANNAF Combustion Meeting, Johns Hopkins University/ Applied Physics Laboratory, Laurel MD, 1-5 October 1984.



Optically Transparent Chamber Configuration for VHBR Studies Figure 8.

An optical study of the combustion of these formulations sheds light on the VHBR combustion mechanism.

The pressure-time history for sample TC-014 (100% TMD) is given in Figure It is seen that there is a slow steady rise in pressure until the blow-out disc ruptured, at 20 MPa. These results are qualitatively similar to those of the closed chamber. A sketch of several frames from the high speed cinematography recordings is shown in Figure 10a. The original color film does not reproduce well enough to show the important details. It may be noted that during the entire combustion sequence, the front surface does not regress, even though the pressure-time hi cay and the gas flow observed in the film indicates substantial gas generation. As time progresses, light from combustion appears further from the front surface of the sample until. finally burning is observed throughout almost the entire sample. At this time, the blow-out disc ruptures and the combustion light disappears. Post firing examination of the chamber revealed a black, porous residue, approximately the same overall dimensions as the original sample. A photograph of the cross section of this residue is shown in Figure 11. From both the high speed films and the residue it is clear that a porous burning of the sample was taking place, and that there was little or no front surface regression. The sample, therefore, was not burning in a laminar, one-dimensional manner. This mode of combustion has been suggested by previous authors.4,

The next sample tested was TC-016 (100% TMD). The density was the same as the previous sample, but it contained 5% binder instead of 15%. Although no quantitative measurements have been made, this material could be cut more readily than TC-014. The pressure-time history is shown in Figure 9. Although faster burning than the TC-014, (100%) sample, it still was slow, consistent with the closed chamber results. A sketch of the high speed cinematography is shown in Figure 10b. This shows the evidence of porous burning, with no front surface regression, but combustion is observed throughout the sample (second from left). A later time sequence of the film (Figure 10b) shows that the combustion front reached the end wall and the remaining propellant was forced towards the blow-out disc, maintaining a cylindrical form. This movement was probably caused by the combustion taking place in the small volume at the end wall, causing the sample to be pushed down the chamber, and out through the blow-out disc. Again, the films show clear evidence of porous combustion.

The pressure-time history for TC-015 (90% TMD) is shown in Figure 12, No. 9. The pressure rises slowly from 22 to 46 ms, increases more rapidly from 46 to 51 ms and rises abruptly from there until both the blow-out disc and chamber ruptured. Figure 13 shows the same run at a higher time resolution (arbitrary time zero). Figure 10c shows a sketch of the high speed films.

^{*}R. Price and J. Ward, "High Burn Rate Propellant as Applied to Recoilless Traveling Charge Gun," Naval Weapons Center Report No. NWC TM 3062, February, 1977.

⁵R.A. Fifer and J.E. Cole, "Transitions from Laminar Burning for Porous Crystalline Explosives," Proceedings Seventh Symposium (International) on Detonation, Naval Surface Weapons Center Report No. NSWC MP82-334, 16-19 June 1984.

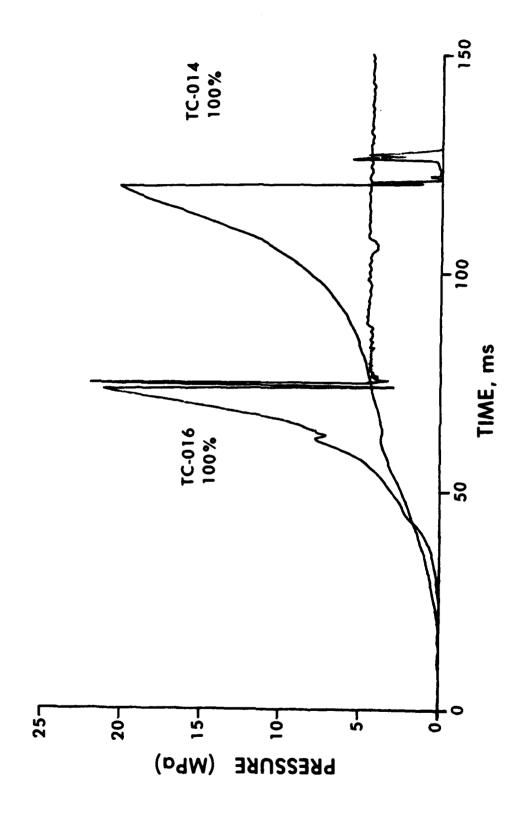


Figure 9. Pressure-time Data for Formulation TC-016 (100% TMD) and TC-014 (100% TMD)

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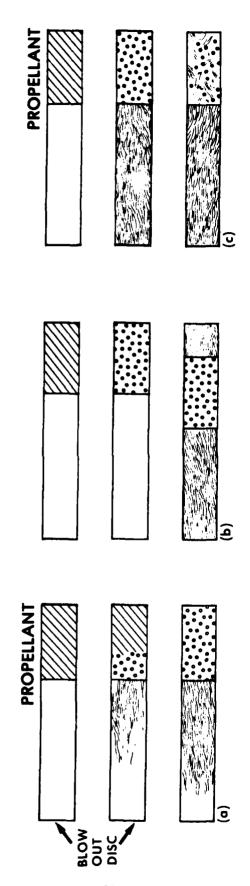
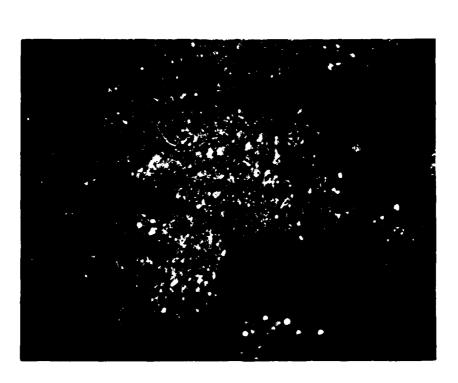
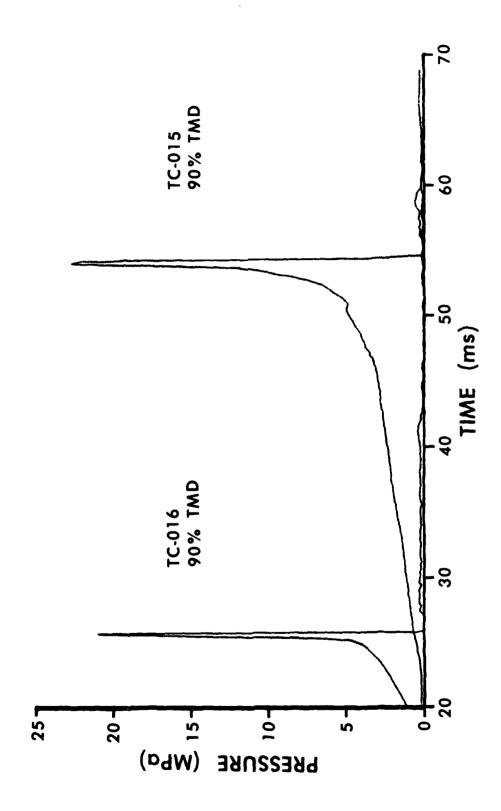


Figure 10. High Speed Cinematography: (a) TC-014/100% TMD, (b) TC-016/100% TMD, (c) TC-015/90% TMD



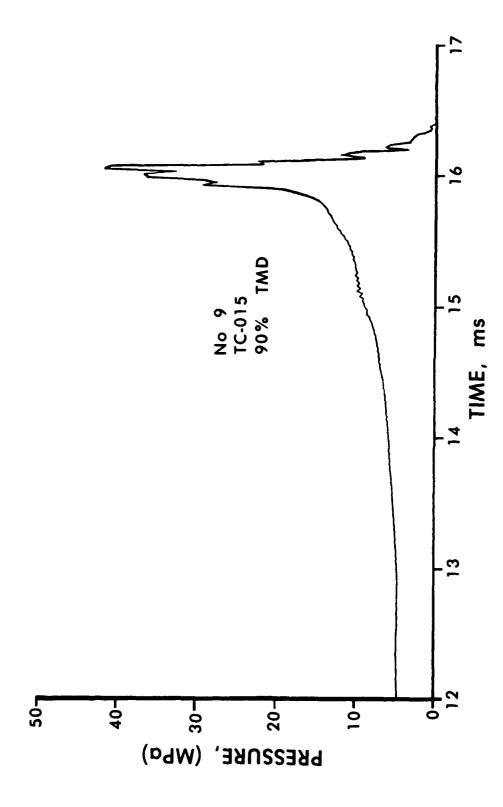
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Figure 11. Post Firing Residue for Formulation TC-014 (100% TMD)



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Figure 12. Pressure-time Data for Formulation TC-016 (90% TMD), and TC-015 (90% TMD)



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Figure 13. Pressure-time Data for Formulation TC-015 (90% TMD), Arbitrary Time Zero.

Porous burning is observed throughout the entire length of the sample without surface regression. In the last frame the sample appears to burn all at once with the chamber rupturing. This coincides with the sudden pressure drop seen in Figure 12.

The fastest burning sample of this series was TC-016 (90% TMD). The pressure-time history is seen in Figure 12. The same observations can be made here as for TC-015 (90% TMD). The sample burns porously with some pressurization and at approximately 5 MPa changes to a very rapid burn/breakup of the entire sample with a sharp rise in dP/dt.

It should be noted here that the expected peak pressure for the loading density used in these tests was between 300 and 400 MPa. As seen in Table II, the transition pressure is less than 7 MPa. Consequently only a few percent of the propellant has burned before the transition to a very rapid burn takes place. Thus, the initial porous burning takes place in only a small volume of the propellant.

C. Conclusions

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The optically transparent chamber results confirm and help explain some of the closed chamber results, and add some insight to the VHBR combustion mechanism. The model postulated here is that these compounds do not burn in a laminar, one dimensional manner, but rather burn porously, at least during the early phases of combustion when only a few percent of the propellant has burned. There is little or no one-dimensional surface regression. This process is relatively slow. After this phase the remaining material (well over 90%) is somewhat porous. If conditions of density/porosity and composition of the original sample are right, the remaining material w'1. burn very rapidly. This transition to the rapid combustion may require pressurization. The porous burning comes about because one or more components of the formulation (for example, the fuel) burn before the others, or burn incompletely, forming pores throughout the sample filled with hot combustion products. If the formulation has some porosity before combustion, say 90% TMD, this will create a large surface area and subsequent rapid combustion. Under these conditions it is difficult to talk about apparent or effective burning rates when bulk or indepth combustion is occurring.

The inherent combustion characteristics of the material may also play a role in the rapid combustion process. Note that the fastest burning formulation in Table II, TC-020 contains an energetic binder. Earlier work has also shown this phenomenon.²

This model is consistent with the closed chamber results. A slow porous burning mode is followed by a transition into a very rapid mode. The slow mode yields a burn rate that increases with pressure (Fig. 3), and the fast mode yields a burn rate that indicates the possibility of a decreasing surface area as the propellant burns (Fig. 4). These arguments were discussed in the section Closed Chamber Studies.

From these relatively slow burning samples a consistent picture of the combustion mechanisms of pressed boron hydride containing formulations has evolved. The data are, however, only a beginning. For faster burning

compositions, such as TC-020, there may be further facets of the mechanism, such as earlier sample breakup or a faster transition from ignition to porous burning. Further diagnostic tests will clarify this situation.

Attempts at replacing the Hivelite fuel with other materials have roven unsuccessful. To produce porous burning, a material with sufficiently different burning characteristics from the rest of the matrix may be required.

At this point all this must be considered to be somewhat speculative, and many questions remain unanswered. What is the effect of sample length on this process? In tests conducted thus far the porous burning reaches the end of the sample before the transition takes place. What will happen with longer samples?

What is the composition of the porous matrix that is left behind after the first phase of combustion? An analysis of this residue, both physical and chemical is important in determining the combustion mechanism of the early porous burning mode. Since porosity can be either closed cell or connected cell, is the type of porosity important in the combustion of these compounds?

Frey³ has seen a strong dependence of high burning rate on the bonding of the sample to the walls of the chamber. Why is this important? We have found that sidewall confinement is necessary for rapid combustion. What role does this play in the transition to rapid burning? Although this is true for many compositions, some very fast burning compositions (such as 1086-5A, see reference 2) require neither pressurization nor circumferential confinement to achieve very fast burning. Thus the role of confinement is not at all clear.

How does the present model explain/fit the thrust bomb data found with a series of VHBR formulations? Can thrust be generated by this mechanism?

The compound with the lower binder content and higher solids loading, TC-016, always burned faster that TC-014 for an equivalent TMD. Are mechanical properties important? Does the transition pressure have anything to do with the pressure dependence of the ignition of some propellant materials? Thus, much work remains to be done, but at this point we have a better understanding of at least the initial steps of how these compounds burn.

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Ol.W. May, F.R. Lynn, A.A. Juhasz, E. Fisher, P.S. Gough, "Thrust Character-ization of Very High Burning Rate Propellants," USA ARRADCOM Ballistic Research Laboratory Report No. ARBRL-MR-03359, July 1984.

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